



<http://www.yambo-code.org>



**TDDFT vs Bethe-Salpeter equation:
ALDA and long-range kernels in
0, 1, 2 and 3 dimensions**

This tutorial describes how to calculate the optical properties of 0/1/2 and 3 dimensional systems in the BS/TDDFT framework.

Before starting the detailed description of the different tutorial examples please read the general remarks about [running yambo](#) in the main documentation page.

Subjects

The basic elements needed in the tutorial are the pre-calculated [yambo input databases](#) and a list of suggested input files, that the user can edit and modify. The input files are labeled by an increasing number that reflects the different level of approximation used

- [01]: [Initialization](#) (command line option `yambo -i`)
- [02-03]: [Random-Phase approximation](#) with and without Local Field effects (`yambo -o c` or `yambo -o b`).
- [04]: [Adiabatic LDA](#) (`yambo -o c -t a` or `yambo -o b -t a`).
- [05]: [RPA static screened interaction](#) (`yambo -b`).
- [06]: [Bethe-Salpeter calculation](#) (`yambo -o b -y dh`).
- [07-08]: A [Long Range model](#) TDDFT xc-kernels (`yambo -o c -t l`)

Getting started

First of all download the [tutorial tarball files](#) and unzip it. Enter the `yambo_tddft_tutorial` directory and you will find five directories corresponding to the systems to be studied plus one directory for the Abinit pseudopotentials:

```
localhost:> ls yambo_tddft_tutorial/  
0D_H2/      1D_Si_wire/      3D_LiF/      2D_Si_surface/      Pseudo_Potentials/
```

In each folder you will find two directories: *Abinit* and *yambo*. In *Abinit* you will find a the input file needed to generate the [KSS](#) file needed by the a(binit)2y(ambo) [interface](#). In the *yambo/SAVE* folder you will also find the [yambo input databases](#) (that can be generated from the KSS files), and in *yambo/Inputs* the input files (01_init, 02_RPA_no_LF, ...). In the *SAVE/Results* folder you can find all the log/report and output files corresponding to the default input files provided.

Note that the yambo input databases (*.db1/*.wf/*.kb_pp) provided have been obtained with an a2y interface compiled with the NETCDF support, so they are readable by yambo in (almost) any platform.

Note that even if the general physical message can be captured using the quick-to-run input files provided a realistic calculation always require careful convergence tests for all the calculation parameters.

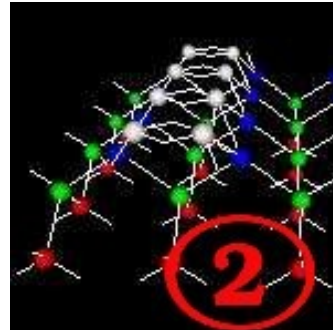
Systems

Click on the material following the order and

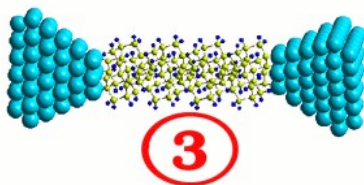
1. check the [conventions](#) page.
2. run all the provided input files following the given instructions.
3. start from the default input files to create new ones in order to solve the questions posed at the end of each page.
4. **To be consistent with the tutorial notation please run any *input_file* using *yambo -F input_file -J input_file*.**



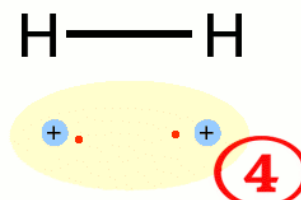
LiF (3D)



Si(111)2x1
(almost 2D)



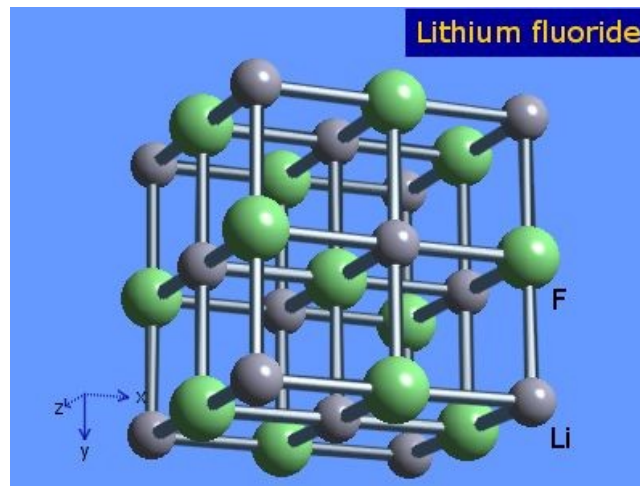
Si Nano Wire
(almost 1D)



Hydrogen molecule
H₂ molecule (0D)

Solid LiF

by Andrea Marini



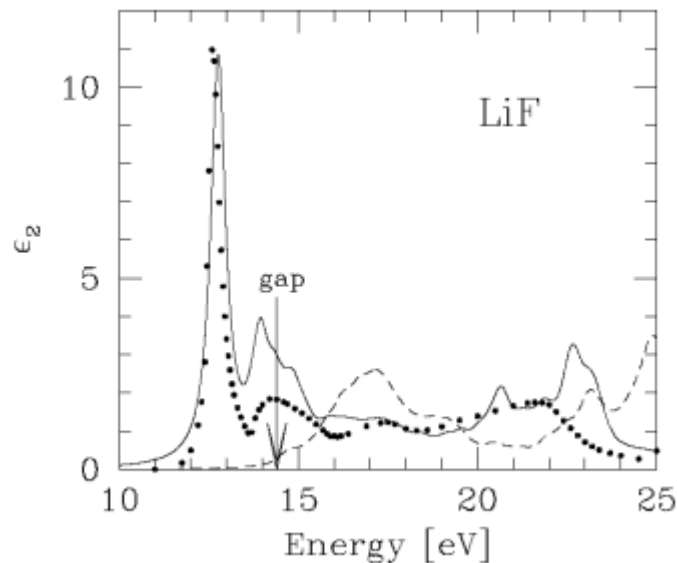
LiF structure.

The material

- FCC lattice
- Two atoms per cell, Li and F (8 electrons)
- Lattice constant 7.61 [a.u.]
- Plane waves cutoff 40 Hartree (1800 RL vectors)

Introduction

We will start the TDDFT tutorial exactly where standard local approximations for f_{xc} (like ALDA) do not work at all. The optical spectrum of solid LiF[1] is dominated by a strongly bound exciton (3 eV binding energy)[2] and will immediately see that any independent particle approximation drastically fail to describe the complex structures that are observed experimentally.




Optical absorption of solid LiF. Dots: experiment. Continuous line: BSE. Dashed line: RPA-QP. See [2] for details.

In the following we will describe in detail the different TDDFT related calculations. For each example you can find a link to the Input file with a brief explanation of the variables

and you will see

```
<---> [01] Game Summary
<---> [02] Input variables setup
<---> RL-shells | _____ | [000%] --(E) --(X)
<---> RL-shells |#####| [100%] --(E) --(X)
<---> [02.01] K-grid lattice
<---> [02.02] Input (E)nergies[ev] & Occupations
<---> [03] Transferred momenta grid: Indexes
<---> [04] Game Over & Game summary
```

If now you edit the *r-01_setup* you will find a lot of useless () informations about your system like, the Fermi level

```
[02.02] Input (E)nergies[ev] & Occupations
=====

Fermi Energy[ev] - T[ev/K] :-0.241627  0.000100  1.160400
Bands summary           : Full      Empty
                        0001-0004  0005-0050
Indirect Gap [ev][min-max]:  9.11330  14.79631
```

confirming that, yes, our bulk LiF is a **wide** gap insulator. Then you can see the effect of using

```
MaxGvecs= 800          RL # [INI] Max number of G-vectors planned to use
```

in the *Inputs/01_init* file. In the report file we notice that

```
G-vectors           [RL space]: 1807
                    [wavefunctions]: 1807
```

whereas the Reciprocal Space shells found by yambo are

```
G-vector (S)hells. Format: [Snn] G`s
[S0030]: 773 [S0029]: 749 [S0028]: 725 [S0027]: 701 [S0026]: 645
[S0025]: 609 [S0024]: 561 [S0023]: 537 [S0022]: 531 [S0021]: 459
[S0020]: 411 [S0019]: 387 [S0018]: 339 [S0017]: 331 [S0016]: 307
[S0015]: 283 [S0014]: 259 [S0013]: 229 [S0012]: 181 [S0011]: 169
[S0010]: 137 [S0009]: 113 [S0008]: 89 [S0007]: 65 [S0006]: 59
[S0005]: 51 [S0004]: 27 [S0003]: 15 [S0002]: 9 [S0001]: 1
```

so that the highest number of RL vectors we can use is 773, lower than the charge number given by Abinit and different from the value for *MaxGvecs* we provided. This happens because yambo has calculated the Reciprocal Space shells up to 800 to find that the highest closed shell corresponds to 773 RL vectors. Note that, independently of the value you set for any variable that defines a dimension in the RL space, yambo redefines it, in order to match it to the nearest closed shell.

[02-03] Random-Phase approximation: [02_RPA_no_LF](#) (yambo -o c) [03_RPA_LF](#)(yambo -o c) [03_RPA_LF_QP](#)(yambo -o c -V 1)

The easiest way of calculating the absorption spectrum of LiF is the [Random Phase Approximation](#) (RPA). In *Inputs/02_RPA_no_LF* a simple RPA calculation is done with

```
NGsBlkXd=1      RL      #      (Xd)      Response block size
```

or, equivalently, neglecting Local Fields Effects (LFE). To run this example type

```
localhost:>yambo -F Inputs/02_RPA_no_LF -J 02_RPA_no_LF
```

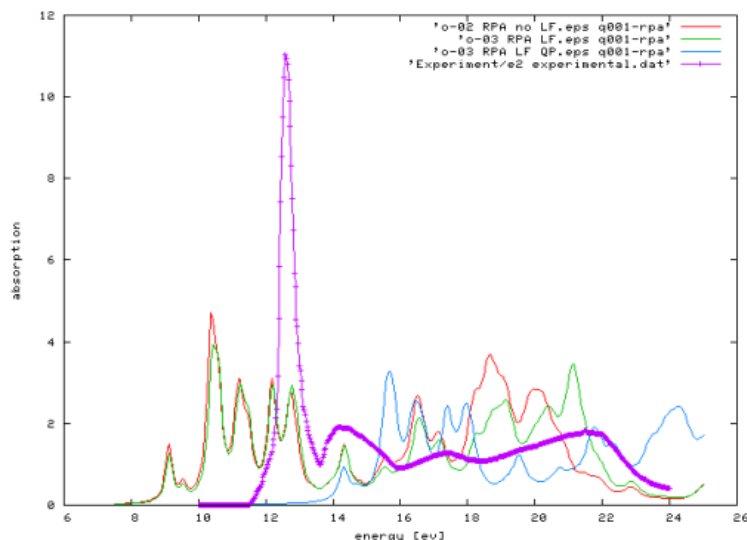
The optional `-J` flag is used to label the output/report/log files (see [here](#) for the command line synopsis).

In `Inputs/03_RPA_LF` the response function size is changed to 51 RL. This means including Local Field Effects corresponding to charge oscillations expanded up to the 51st RL component. The converged value for `NGsBlkXd` shall be determined by doing several calculations with different values and checking the effect on the final physical result (the absorption spectrum, in this case).

After having run

```
localhost:>yambo -F Inputs/03_RPA_LF -J 03_RPA_LF
```

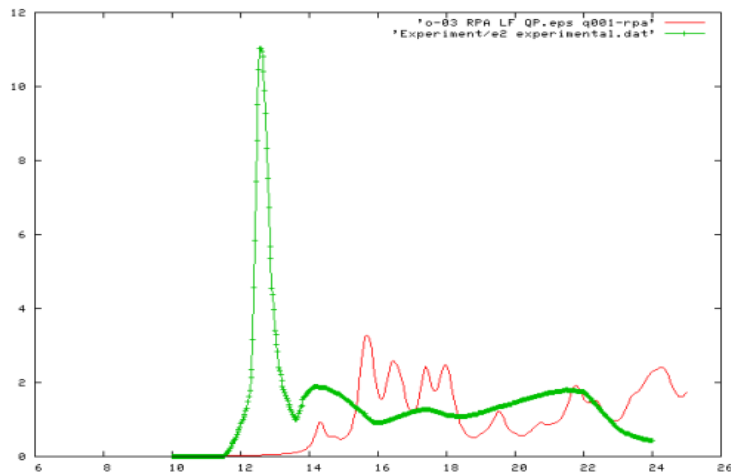
we can compare the result of our calculations with the experimental curve (that you find in the `Experiment` folder).



The comparison with the experiment clearly show that the RPA is not at all adequate in the case of LiF. We notice two main discrepancies between theory and experiment: the RPA absorption onset is too low and the shape lacks the sharp peak observed experimentally at around 12 eV. The onset position can be artificially corrected using a scissor operator (representing the QP gap correction) of 5.19 eV that simply opens rigidly the LDA gap. This is shown in `Inputs/03_RPA_LF_QP` with the line

```
% XfnQP_E  
5.190000 | 1.000000 | 1.000000 | # [EXTQP Xd] E parameters (c/v)  
%
```

The resulting spectrum fits better with the experiment but now there seems to be an even more serious problem:



there is an experimental peak well below the QP absorption onset:

an EXCITON!

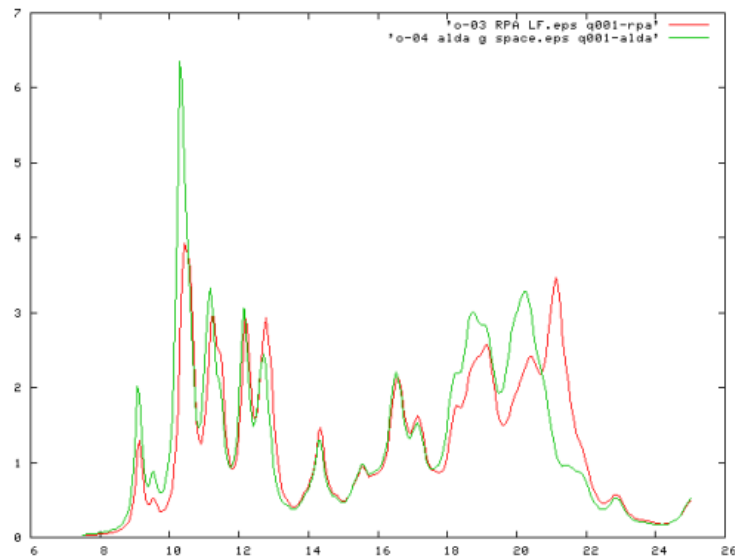
[04] ALDA: 04_ALDA_g_space(yambo -o c -t a)

Our first attempt to go beyond RPA is using [TDDFT](#) in the Adiabatic LDA approximation. Depending on the exchange-correlation(xc) functional used in the ground state calculation yambo will produce a corresponding xc-kernel. In this case, as reported by the `a2y` command we are using a Perdew Wang parametrization.

Running

```
localhost:>yambo -F Inputs/04_alda_g_space -J 04_alda_g_space
```

we get



Unfortunately ALDA only slightly changes the RPA result. The situation will change in more isolated system (reduced dimensionality).

[05] The Statically screened Electron-electron interaction: 05_W(yambo -b)

As simple RPA and ALDA approximations have not described correctly the experimental spectrum we have to move towards more elaborate techniques like the Bethe-Salpeter

(BS) equation.

A key ingredient in the [BS kernel](#) is the electron-electron interaction commonly evaluated in the [static](#) approximation. The input file *Inputs/05_W* describes how to calculate it. The variables used in this input file have the same physical meaning of those used in the optical absorption calculation. The only difference is that, in general, the response function dimension obtained in the examples (03-04), gives an upper bound to the number of RL vectors needed here. This is because the size of response matrix in an RPA calculation defines also the size of the Hartree potential, whose short-range components are not screened. In the present case, instead, the electron-electron interaction is screened and, for this reason, the RL vectors needed are considerably smaller than in the RPA case. So let's type (no *-J* option here) ...

```
localhost:>yambo -F Inputs/05_W
```

... and after waiting for some minutes the result, that is the [database SAVE/ndb.em1s](#). Here it is better to skip the *-J* option as we will need to read this database in the next examples.

[06] The Bethe-Salpeter equation, Excitons: [06_BSE](#)(yambo -o b -y h)

The input file *Inputs/06_BSE* describes how to calculate an excitonic absorption spectrum, using as a solver of the BS equation the [recursive Haydock Method](#). Before running *yambo* we must have a closer look at the input file:

The line

```
% KfnQP_E
 5.80000 | 1.000000 | 1.000000 |      # [EXTQP BSK BSS] E parameters (c/v)
%
```

applies a 5.8 eV scissor in order to open the LDA gap.

```
BSresKmod= "xc"          # [BSK] Resonant Kernel mode. (`x`;`c`;`d`)
```

Here we are doing a BSE calculation including both exchange and correlation terms in the [resonant part](#) only of the kernel as the coupling part generally induces a small effect in semiconductors and insulators. We will see the effect of the coupling term in the H₂ molecule.

```
% BSEBands
 2 | 7 |          # [BSK] Bands range
%
BSENGBlk= 51      RL # [BSK] Screened interaction block size
BSENGexx= 773    RL # [BSK] Exchange components
```

Here we specify the range of bands to be used and the RL components for the screened interaction (51) (read from the *ndb.em1s* file) and for the Hartree term (773, the maximal available). **Remember** that the BS kernel is written in Bloch space and its size is given by
BS kernel size = Valence Bands × Conduction Bands × K-points in the whole BZ

In our case the size is 2304. The BS bands range must be converged with care trying to keep as a few bands as possible.

Running

```
localhost:>yambo -F Inputs/06_BSE -J 06_BSE
```

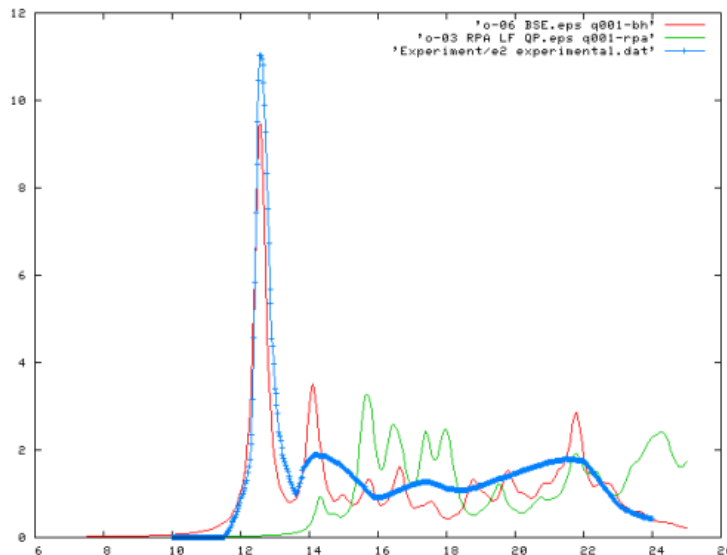
will calculate the BS kernel and store in in the *06_BSE* folder. Before analyzing the BS

absorption spectrum we can edit the log file *I-06_BSE_optics_bse_bss* to observe the on-the-fly live timing feature of yambo:

```
[...]
<---> BSK | | [000%] --(E) --(X)
<05s> BSK |# | [007%] 05s(E) 01m-07s(X)
<11s> BSK |### | [015%] 10s(E) 01m-06s(X)
[...]
<01m-02s> BSK |##### | [093%] 01m-01s(E) 01m-06s(X)
<01m-07s> BSK |##### | [100%] 01m-06s(E) 01m-06s(X)
[...]
```

The two numbers at the end of each line represents the elapsed time(E) and the expected time(X). The latter estimates the time needed to complete that particular section (the BS kernel construction in this case).

Finally we can compare the resulting BS optical absorption with the experimental result. We see how strong is the excitonic effect, if compared to the RPA calculation. The BS equation is, then, able to describe the bound electron-hole state responsible for the peak observed experimentally below the QP gap.

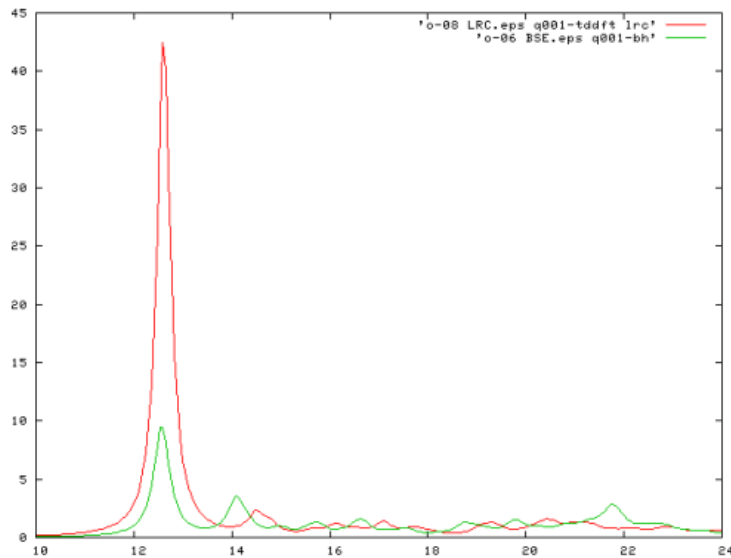


[07] A Bethe-Salpeter based F_{xc} : [07_LRC](#)(yambo -o c -t l)

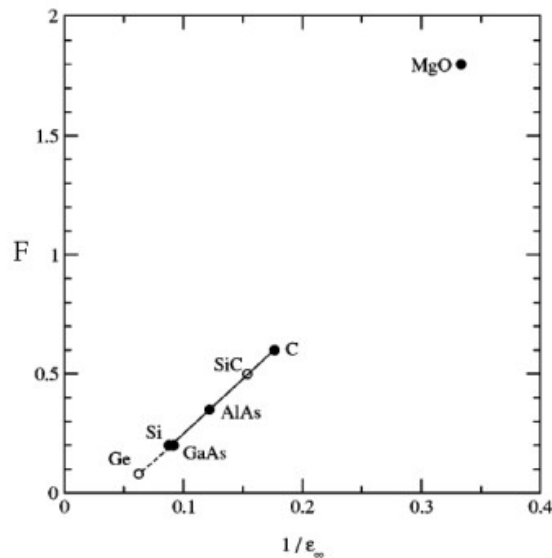
As the subject of this tutorial is TDDFT we might be a little bit disappointed at this stage as the only method that yields a reasonable absorption spectrum for LiF is based on MBPT. It is possible, however, to extract from the BS kernel a possible approximation for the xc-kernel, as described [here](#). This approach is efficient, but is far too complicated, and requires the prior computation of the BS kernel. An alternative possibility is to use a simple [Long Range Component](#) model, as introduced in [Reining](#). In this model, the yambo input file *Inputs/07_LRC* describes a model where

$$f_{xc}(\mathbf{r}, \mathbf{r}') \equiv \frac{F_0}{|\mathbf{r} - \mathbf{r}'|}$$

with $F_0 = LRC_alpha = -8.7$.



We see from the previous figure that the agreement with the BS calculation is not very good. Nevertheless this simple model captures the presence of an exciton and works quite well for a large number of simple semiconductors, as show in [Botti](#):



For a more detailed and careful discussion of the LRC kernel, have a look at the [Hydrogen chain tutorial](#).

Additional Exercises

1. Calculate the absorption spectra like in section [02-03](#) increasing the polarization RL size, the polarization bands to find the converged values.
2. Plot the EELS spectrum obtained in section [02-03](#) and check the effect of increasing the polarization bands. Do a resonant only calculation (using the -V option) to see that the EELS cannot be described using only the resonant part of the response function.
3. See the effect of using a denser BZ sampling grid running Abinit with, for example `ngkpt2 6 6 6`
4. Repeat the [BSE](#) calculation increasing the bands.
5. Calculate the [BSE](#) spectrum using a diagonal only interaction (see [here](#)).

Si(111)2x1 surface

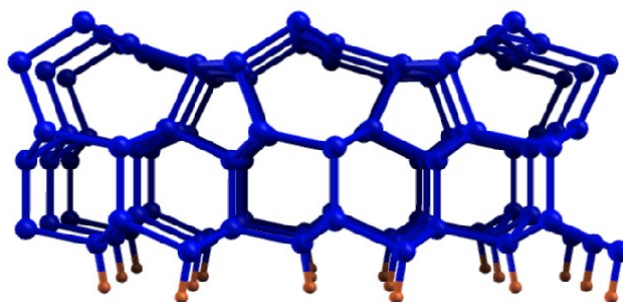
by Andrea Marini & Maurizia Palumbo

The material

- Repeated slab approach: 6 layers of silicon plus 5 a.u. of vacuum region.
- 14 atoms in the cell (50 electrons)
- Plane waves cutoff 6 Hartree (2400 RL vectors)

Introduction

The Si(111)2x1 surface is characterized by the famous *Pandey* reconstruction [1], done by bonded chains of Silicon atoms along the [01-1] direction



Large blue spheres represent Si atoms; small red spheres are hydrogen atoms used to saturate the dangling bonds. On the bottom the ideally terminated surface.

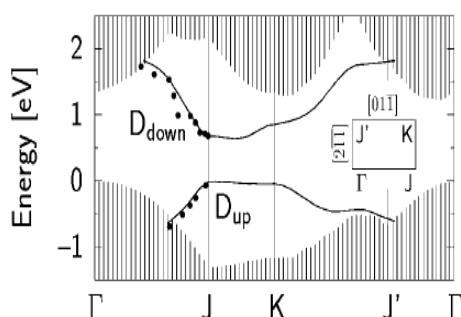


Fig.(2). Electronic bandstructure of the Si(111) 2x1 surface from [2]. The shaded areas denote Si bulk states. The continuous lines indicate the dispersion along the high-symmetry directions of the Brillouin Zone of the occupied and unoccupied surface states, which are the states involved in the optical peak observed at about 0.45 eV. The dots are experiments. See [2] for details.

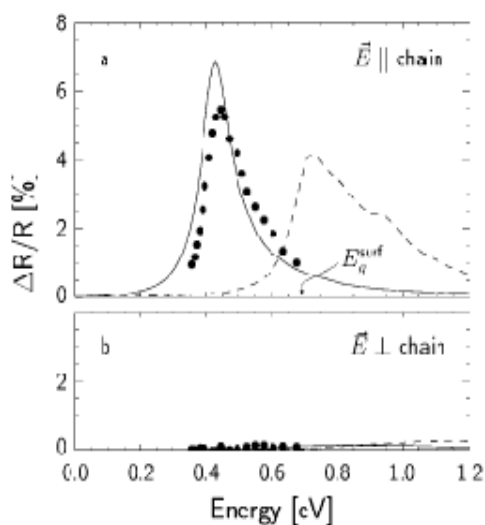


Fig.(3). Differential reflectivity theoretical spectrum of the Si(111)2x1 surface, compared with experiments (dots) [2]. The dashed curve is the theoretical spectrum obtained at the RPA-GW level, while the solid curve is obtained solving the BSE equation, with the inclusion of self-energy, local-fields and electron-hole interaction. Top panel for light polarized along the Pandey chains, bottom panel for light polarized perpendicular to them.

The electronic band-structure and optical properties within first-principles, using the GW method and the *BSE* approaches, have been calculated in the past years [2] and explain the experimental optical peak observed in the experiments [3] at about 0.45 eV, as due to a surface-states exciton, bound about 0.25 eV. From an historical point of view, it is interesting to mention that its measurement was one of the first experimental proofs of the existence of surface states in semiconductor surfaces.

Before starting with the calculations let us say few words about the experimental data we wish to compare with. The optical data reported in the previous figure, have been obtained using a Surface Differential Reflectance (SDR) technique. In this optical spectroscopy the reflectance of the clean surface is measured first, and then that of the surface after chemisorption of some adsorbate (generally hydrogen or oxygen); the difference, the SDR, a few percent of the reflectance, surely originates at the surface. The use of this optical spectroscopy or other ones, such as the Reflectance Anisotropy Spectroscopy (see ref. [4] for an extended discussion), is required to make the optical probe, due to its large penetration, sensitive to the surface region. This means that, in order to compare properly with the experiments, we should calculate the reflectance for the clean and the covered Silicon surface following the formulas given, for instance, in ref [4]. Nevertheless, in the present case, the SDR signal at about 0.45 eV, (present only for light polarized along the Pandey chains, top panel), is actually proportional to the polarizability of the clean surface. For this reason, in the present tutorial, we will limit to calculate only the slab polarizability, for light polarized along the Pandey chains and perpendicular to them, and we will compare the first one with the experimental SDR peak, simply rescaling its intensity.

In order to simulate the surface/vacuum system the repeated slab approach is used. In the present simulation we have: an atomic slab of 6 layers of Silicon (with one of the surfaces presenting the Pandey reconstruction, while the other one has an ideal termination, with the Silicon dangling bonds saturated by Hydrogen atoms) and a vacuum region of about 5 a.u., in order to eliminate the spurious interactions among the images in the different cells; a uniform bi-dimensional mesh of 13 k-points in the IBZ.

It is important to underline that the atomic slab and vacuum thickness, k-point mesh, and kinetic energy cut-off (only 6 Hartree) are not appropriate for a well converged calculation, but have been chose, here, to speed up the simulations.

[01] Initialization: [01_init](#)(yambo -i -V 1)

To run this example enter the *2D_Si_surface/yambo* directory and type

```
localhost:>yambo -F Inputs/01_init
```

Note the use of only 1000 RL components instead of the 2400 available from the DFT charge

```
MaxGvecs=1000          #          (INI)      Max number of G-vectors planned to use
```

[02-03] Random-Phase approximation: [02_RPA_no_LF_par](#)(yambo -o c) [02_RPA_no_LF_perp](#)(yambo -o c) [03_RPA_LF](#)(yambo -o c) [03_RPA_LF_QP](#)(yambo -o c -V 1)

The easiest way of calculating the slab polarizability tensor (here we will calculate only the two needed components, for light polarized along the Pandey chains and perpendicular to them) is the [Random Phase Approximation](#) (RPA). The *Inputs/02_RPA_no_LF_par* and *Inputs/02_RPA_no_LF_perp* are the inputs for simple RPA response function calculations without the inclusion of Local Field Effects (LFE), for light polarized along

```
% LongDrXd
0.000000 | 1.000000 | 0.000000 |          # [Xd] [cc] Electric Field
```

%
and perpendicular to the Pandey chains

```
% LongDrXd
1.000000 | 0.000000 | 0.000000 |          # [Xd] [cc] Electric Field
```

%

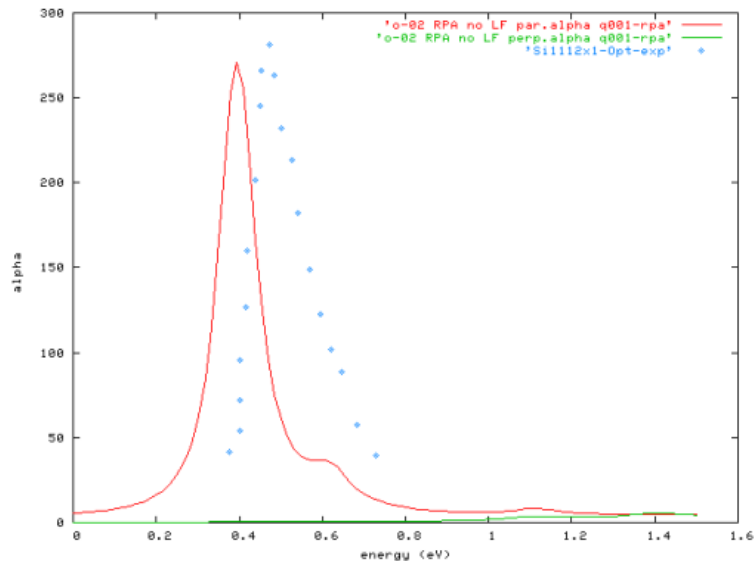
with

NGsBlkXd=1 RL # (Xd) Response block size

To run these two examples, type:

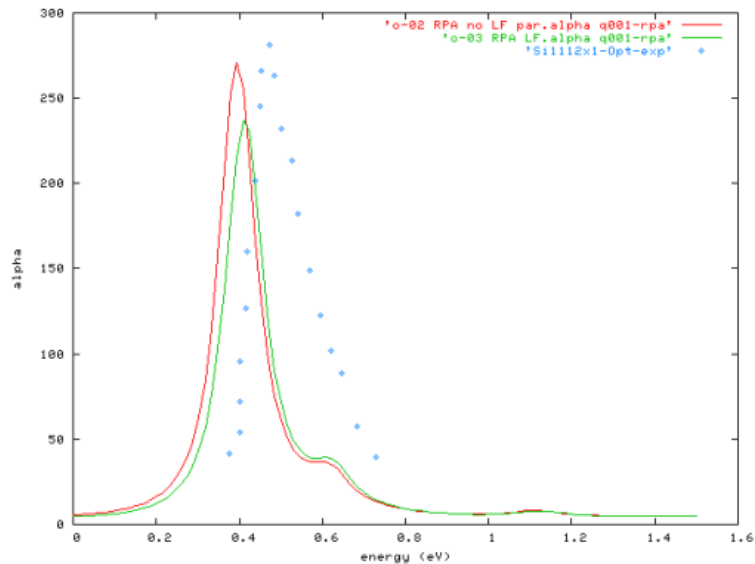
```
localhost:>yambo -F Inputs/02_RPA_no_LF_par -J 02_RPA_no_LF_par  
localhost:>yambo -F Inputs/02_RPA_no_LF_perp -J 02_RPA_no_LF_perp
```

After running, we should compare the obtained theoretical curves with the experiments. The comparison looks like:



You can see, already at the simple RPA level, evidence of the strong anisotropy of the optical peak due to surface-surface states transitions, which is completely polarized along the Pandey chains. We can note that, since we are neglecting the many-body effects, the energetic position of the optical peak (for light polarized along the Pandey chains) is not in good agreement with the experiments. Furthermore it is important to underline that actually the disagreement increases, performing a well converged RPA calculation (denser k-points mesh, higher kinetic energy cut-off, thicker slab).

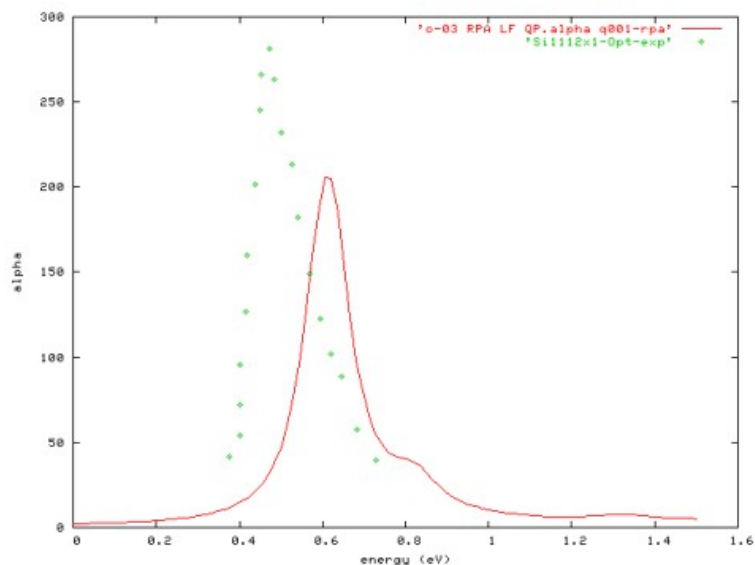
We can see now, which is the effect to include more G-components in the response function (in other words, include Local Field Effects) for the polarizability for light polarized along the Pandey chains. In *Inputs/03_RPA_LF_par* the response function size is changed to 50 RL. The converged value for *NGsBlkXd* must be found doing several calculations with different values and checking the effect on the final spectrum. After running, you should obtain the following curves:



Again the comparison with the experiment clearly show that the LF effects are not enough to have a good agreement with the experiments. The onset position can be artificially corrected using a QP gap correction of 0.2 eV that simply opens rigidly the LDA gap. This is done in *Inputs/03_RPA_LF_QP* with the line

```
% XfnQP_E
0.20000 | 1.000000 | 1.000000 | # [EXTQP Xd] E parameters (c/v)
%
```

and the corresponding result looks like:



[04] ALDA: [04_ALDA_r_space](#)(yambo -o b -t a)

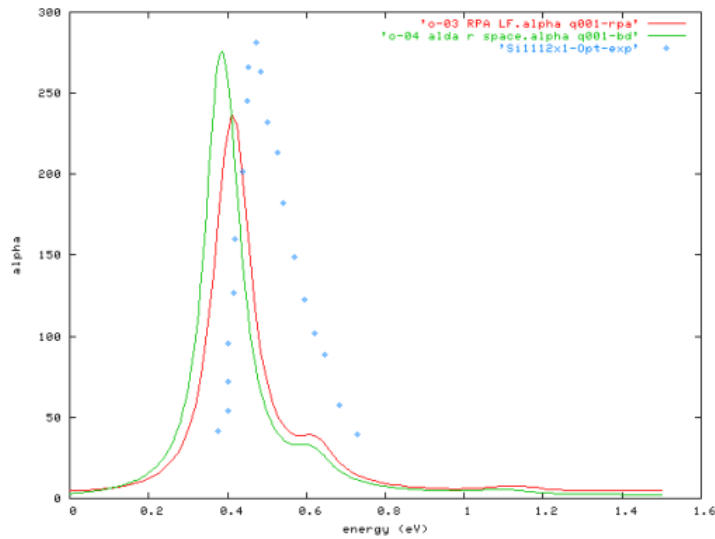
Again the first attempt to go beyond RPA is to use the [TDDFT](#) in the Adiabatic LDA approximation.

The input file *Inputs/04_alda_r_space*, at difference with the bulk LiF case, uses the [Bloch representation](#) of the TDDFT equation. In this case yambo uses the Bethe-Salpeter equation with a modified exchange part that includes the ALDA kernel.

To run this example, type:

```
localhost:>yambo -F Inputs/04_alda_r_space -J 04_alda_r_space
```

After running, we can compare again the theory and the experiment and see that ALDA gives only slightly changes to the RPA (with LFE) result.



[05] The Statically screened Electron-electron interaction: 05_W(yambo -b)

As we have seen, in other sections of this tutorial, the calculation of the statically screened Electron-electron interaction is required in order to perform a Bethe-Salpeter calculation. To perform this calculation, type:

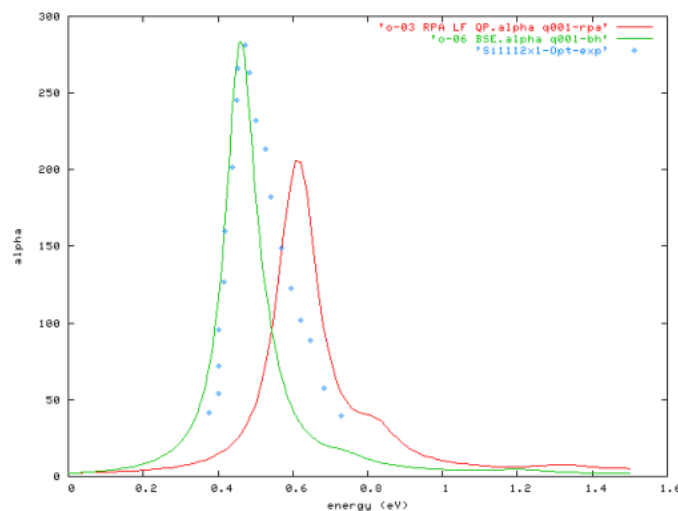
```
localhost:>yambo -F Inputs/05_W
```

The screened interaction matrix will be written at the end of this run in the database SAVE/ndb.em1s. It is important to underline that, also at this level of the calculation, careful convergence tests in the plane-wave components and the electronic transitions involved in the screened coulomb interaction matrix, should be, in principle, required.

[06] Bethe-Salpeter equation 06_BSE(yambo -o b -y hd)

We are now ready for a BSE calculation, the hope is to obtain now, with the inclusion of the excitonic effects, an optical spectrum (for light polarized along the Pandey chains) which can compare well with the experiments. To see what happens, type:

```
localhost:>yambo -F Inputs/06_BSE -J 06_BSE
```



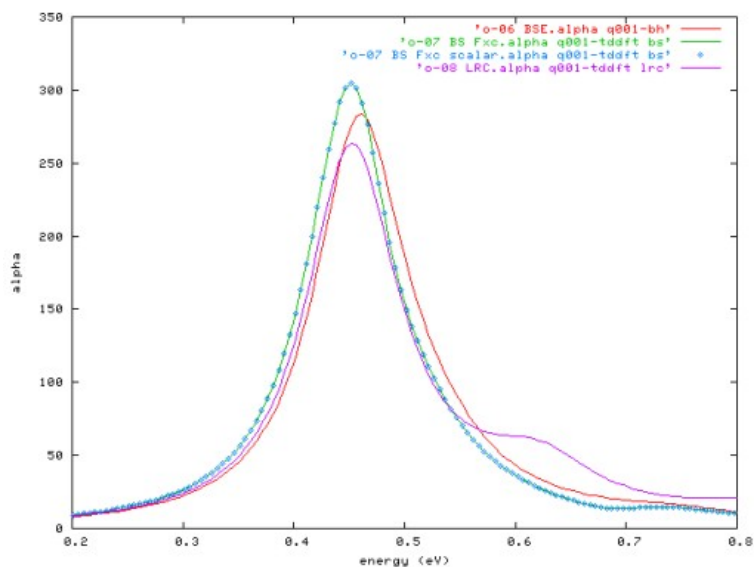
We can see that the BS equation is, also in this case, able to give a theoretical optical spectrum in nice agreement with the experiments, describing the bound electron-hole state responsible for the peak observed experimentally below the QP gap (see Fig.2 from ref. [2], for well converged GW and BSE calculations). This surface-states exciton is clearly much less bound than in the case of the LiF, but we have to consider that Silicon is a small gap semiconductor and actually the corresponding binding energy in the bulk Silicon is completely negligible.

[07] A Bethe-Salpeter based F_{xc} : [07_LRC\(yambo -o c -t l\)](#)

As in the case of LiF, you can try, also in this surface, a simple Long Range Component model, as introduced in [Reining](#) using the input file *Inputs/07_LRC* where

```
LRC_alpha= -0.280000      # [TDDFT] LRC alpha factor
```

The resulting optical spectra, compared with BSE curve, are the following:



We see from this last figure that (at least for this low energy optical peak of the Si(111)2x1 surface) the agreement with the BS calculation is actually very good, and the simple Long Range Component model properly describes this bound exciton.

Additional Exercises

1. Calculate the polarizability including local fields effects for light polarized perpendicular to the Pandey chains.
2. Repeat the calculations of the polarizability spectra of section [02-03](#) using the Bloch representation of TDDFT (yambo -o b -y d).
3. Repeat the [ALDA](#), [BSE](#), and [LRC](#) calculations for light polarized perpendicular to the Pandey chains.

Si(111) hydrogenated wire

by Andrea Marini & Maurizia Palumbo

The material

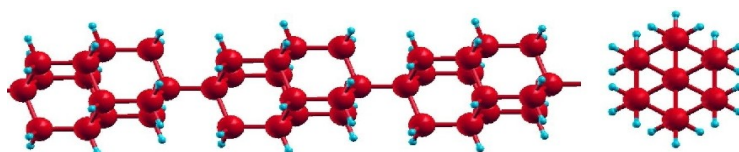
- The wire is along the x direction.
- 32 atoms in the cell (74 electrons)
- Plane waves cutoff 8 Hartree (10500 RL vectors)

Introduction

Nanostructuring of semiconductors is an alternative means of developing new electronic and opto-electronic devices. The huge efforts made towards matter manipulation at the nanometer scale have been motivated by the fact that desirable properties can be generated just by changing the system dimension and shape. In particular, the possibility of tuning the optical response of nanosized materials by modifying their size has become one of the most challenging aspects of recent semiconductor research. Among the different nanostructures, nanowires have recently attracted a lot of interest. Being one-dimensional structures, they seem potentially useful as well as the Carbon-nanotubes and probably more, due to the possibility to tailor their chemistry and to be used to create nano-sized lasers. They exhibit extreme quantum confinement effects such that charge carriers are free to move only along the wire. The knowledge of the electronic and optical properties of Silicon nanowires is of particular interest due to their natural compatibility with silicon based technologies, and due to the discovery of photoluminescence in the visible range in Porous Silicon and in quantum matrices of Silicon. Here we aim to examine how the quantum-confinement and how local-fields and excitonic effects influence the optical spectrum of a very thin ($D=4 \text{ \AA}$) Silicon nanowire, grown along the 111 crystallographic direction.

Considerations similar to the other sections of this tutorial, about convergence parameters, have to be done. In fact a small kinetic energy-cutoff, a sparse k-points mesh, and a small number of unoccupied bands are used here, in order to speed up the calculations. Nevertheless the main physical features will be captured, such as: the importance of local-field effects for the light polarization perpendicular to the wire axis [1], and the presence of strongly bound excitons about 2 eV [2].

Although this tutorial is not dedicated to the quasi-particle electronic structure calculations within the GW method, it is important to mention that in these 1-D subnanometer systems, one of the recent findings (see refs. [2],[3], for more details) is that the self-energy corrections to the DFT-KS eigenvalues increase as the wire size is decreased. In particular for the wire studied here a self-energy correction more than 3 times larger than the value obtained in the Silicon bulk is found[3]. Furthermore before starting the simulation we have to underline that for nanowires the comparison with the experiments is, unfortunately, not so straightforward. In fact, from an experimental point of view, it is very difficult to grow monosized wires, with a well characterized morphology and surface reconstruction. The main interest should be to study the trend of the electronic and optical properties by changing the size, the orientation and the morphology of the nanowire. This cannot clearly be done here and you will not find any experimental curve in the following... sorry!!!



Lateral and top view of the Si(111) wire. Large red spheres represent Si atoms; small blue spheres are hydrogen atoms used to saturate the dangling bonds.

[01] Initialization: [01_init](#)(yambo -i -V 1)

To run this example enter the *1D_Si_wire/yambo* directory and type

```
localhost:>yambo -F Inputs/01_init -J 01_init
```

[02-03] Random-Phase approximation: [02_RPA_no_LF_par](#)(yambo -o c), [02_RPA_no_LF_perp](#)(yambo -o c), [03_RPA_LF_par](#)(yambo -o c), [03_RPA_LF_perp](#)(yambo -o c), [03_RPA_LF_QP_par](#)(yambo -o c -V 1)

As we have learned in the other sections of this Tutorial, the easiest way to calculate the optical properties, is to perform a [Random Phase Approximation](#) (RPA) calculation without the inclusion of LFE. We will calculate here the two components of the polarizability tensor of the wire, for light polarized along the wire axis and perpendicular to it. We will see that, already at this independent particle level, the optical response is strongly anisotropic. Furthermore we will find that the onset is blue shifted with respect to the RPA optical spectrum of the bulk Silicon and this is actually due to Quantum Confinement effect.

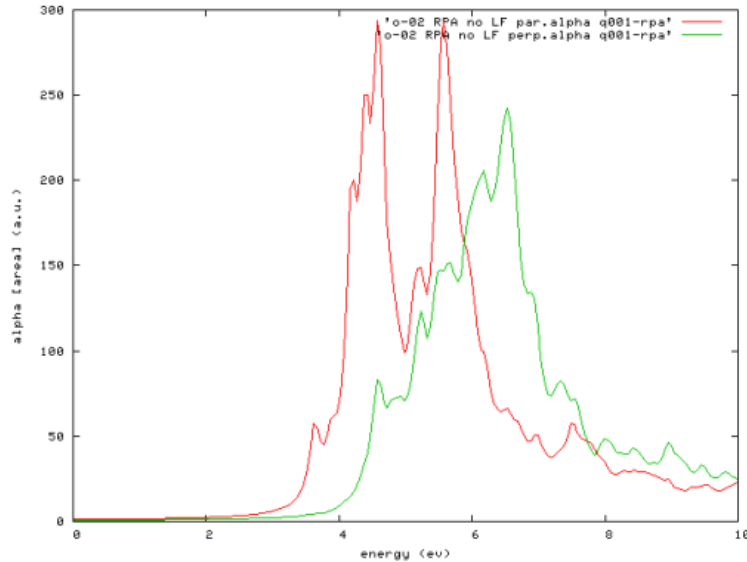
The *Inputs/02_RPA_no_LF_par* and *Inputs/02_RPA_no_LF_perp* are the inputs for simple RPA response function calculations without the inclusion of Local Field Effects (LFE), for light polarized along and perpendicular to the wire's axis, with

```
NGsBlkXd=1    RL    #    (Xd)    Response block size
```

To run these two examples, type:

```
localhost:>yambo -F Inputs/02_RPA_no_LF_par -J 02_RPA_no_LF_par
localhost:>yambo -F Inputs/02_RPA_no_LF_perp -J 02_RPA_no_LF_perp
```

After running, you should obtain the following curves:

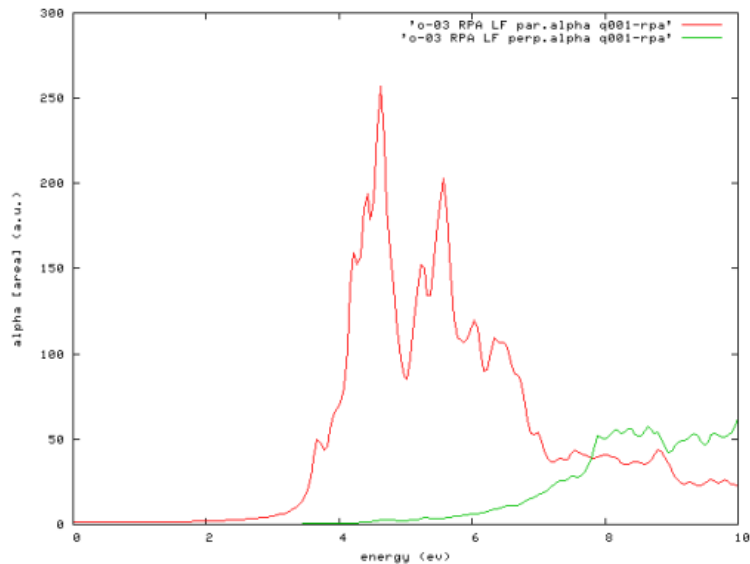


We can now see, the effect of including more RL components in the response function (in other words, by including Local Field Effects) for the polarizability for light polarized along the wire axis (*Inputs/03_RPA_LF_par*) and perpendicular to it (*Inputs/03_RPA_LF_perp*).

In these input files, the response function size is changed to 107 RL. The converged value for *NGsBlkXd* must be found doing several calculations with different values and checking the effect on the final spectra. After running

```
localhost:>yambo -F Inputs/03_RPA_LF_par -J 03_RPA_LF_par
localhost:>yambo -F Inputs/03_RPA_LF_perp -J 03_RPA_LF_perp
```

we will find

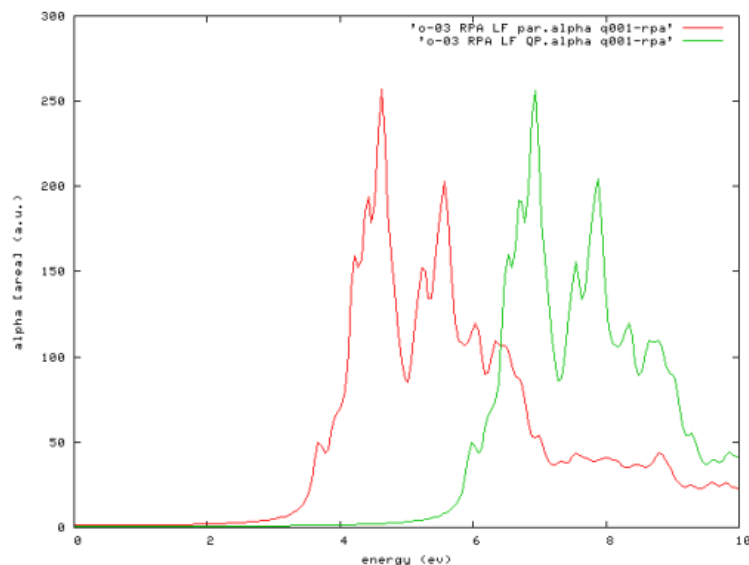


This Figure illustrates how the optical response of the wire is modified by taking into account the inhomogeneity of the system. Similar to other one-dimensional systems, such as carbon nanotubes, when local field effects are included [4], an important intensity reduction is observed for perpendicular light polarization which renders the wire almost transparent up to about 7 eV, while a small change of the optical spectrum for light polarized along the wire axis. This depolarization effect, which originates from the presence of microscopic electric fields due to the induced polarization charges after the application of the external field, has been actually observed experimentally both in nanotubes and in porous silicon matrices (see references [2],[4] for more details). Moreover, as explained in ref [1], the observed anisotropy can be almost entirely explained in classical terms by using Effective Medium Theory (EMT) formulas.

GW calculations [3] have shown that the self-energy corrections open the DFT gaps of about 2.3 eV. For this reason we can use here such a value as a scissor operator which simply opens rigidly the LDA gap. This is done in *Inputs/03_RPA_LF_QP* with the line

```
% XfnQP_E
2.30000 | 1.000000 | 1.000000 | # [EXTQP Xd] E parameters (c/v)
%
```

and the corresponding result (we consider here only the polarizability for light polarized along the wire axis) looks like:



[04] ALDA: [04_ALDA_g_space\(yambo -o c -t a\)](#), [04_ALDA_r_space\(yambo -o b -t a\)](#)

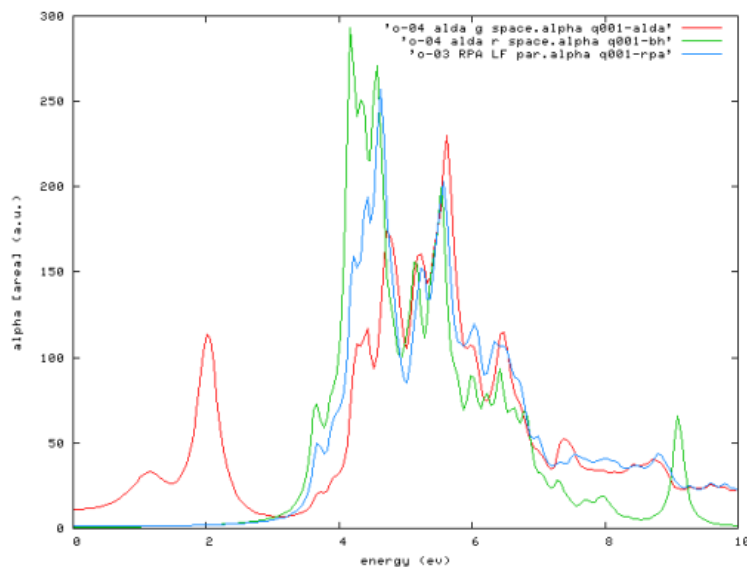
Again the first attempt to go beyond RPA is to use the [TDDFT](#) in the Adiabatic LDA approximation. As we have learned, with yambo, we can run this kind of calculation, both in the RL (*Inputs/04_alda_g_space*) and in the Bloch space implementation (*Inputs/04_alda_r_space*).

To run these two cases, type:

```
localhost:>yambo -F Inputs/04_alda_g_space -J 04_alda_g_space
```

```
localhost:>yambo -F Inputs/04_alda_r_space -J 04_alda_r_space
```

As you can see from the next figure, the RL implementation yields a wrong polarizability, **with spurious states below the absorption gap**. This anomalous effect is not present in the Bloch-space implementation, and it is due to the fact that in isolated systems (like the Si wire) there are large regions where the charge is very small. In these regions the ALDA f_{xc} kernel diverges and the multiplication in RL space with the non-interacting response function (which vanishes) is numerically unstable. On the contrary the Bloch-space implementation properly works, inducing small but visible changes with respect to the RPA spectrum. Nevertheless the ALDA will not be able to reproduce the BSE curve, the we will calculate in the next sections.



[05] The Statically screened Electron-electron interaction: [05_W\(yambo -b\)](#)

As we have seen, in other sections of this tutorial, the calculation of the statically screened Electron-electron interaction is required in order to perform a Bethe-Salpeter calculation. To perform this calculation, type:

```
localhost:>yambo -F Inputs/05_W
```

The screened interaction matrix will be written at the end of this run in the database `SAVE/ndb.em1s`. It is important to underline that, also at this level of the calculation, careful convergence tests in the plane-wave components and the electronic transitions involved in the screened coulomb interaction matrix, should be, in principle, required.

[06] Bethe-Salpeter equation 06_BSE(yambo -o b -y h)

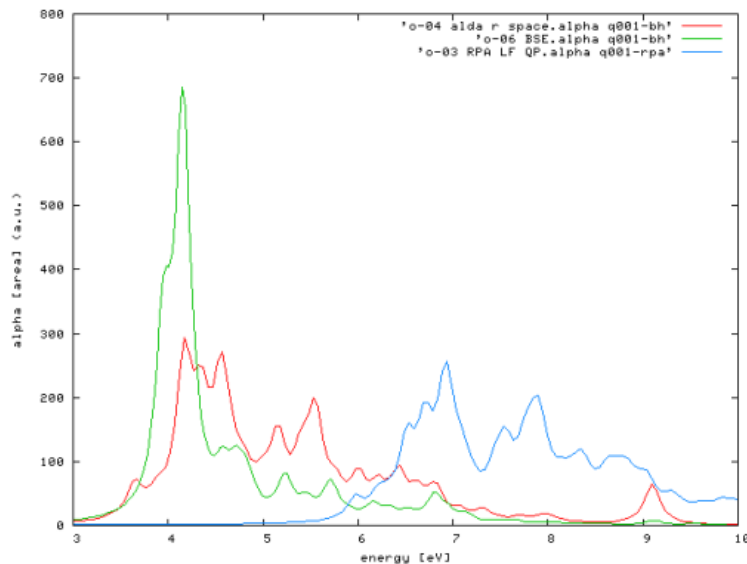
We are now ready for a BSE calculation. In particular we aim to see here, how the excitonic effects influence the optical spectrum for light polarized along the wire.

To run the BSE calculation, type:

```
localhost:>yambo -F Inputs/06_BSE -J 06_BSE
```

We should find that, also the effect of the electron-hole interaction on the optical properties of the wire, strongly depends on light polarization: for light polarized perpendicular to the wire axis, the BSE optical spectrum will be rather similar to the RPA curve when LFE are introduced, whereas for light polarized along the growth axis, a transfer of the oscillator strength to the low energy peaks is observed together with a reduction of the intensity above the electronic gap.

The BSE spectrum (blue curve) for light polarized along the wire's axis, compared with the spectra obtained at the quasi-particle (green curve) and at the ALDA (red curve) levels, looks like the following:

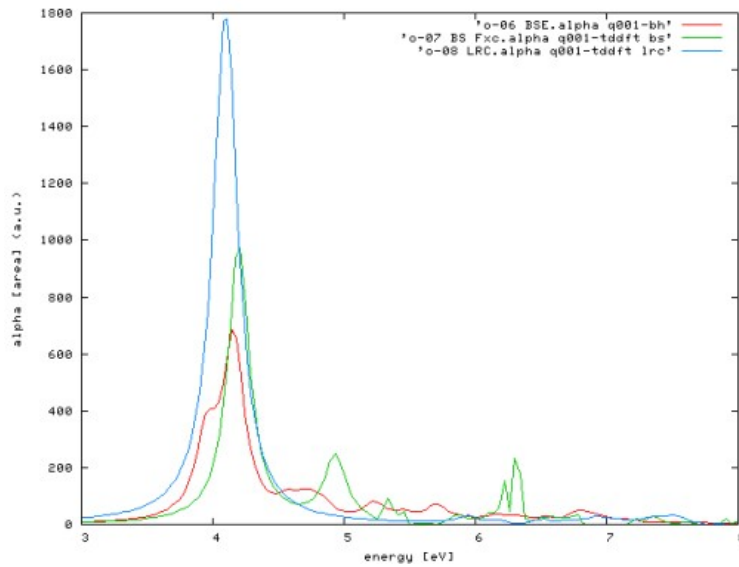


[07] A Bethe-Salpeter based F_{xc} : 07_LRC(yambo -o c -t l)

Last of all, you can try the simple Long Range Component model, as introduced in [Reining](#) using the input file *Inputs/07_LRC*. Here we set

```
LRC_alpha= -9.50000 # [TDDFT] LRC alpha factor
```

much larger than in the surface case (consequence of the reduced dimensionality).



Additional Exercises

1. Calculate the polarizability spectra like in section [02-03](#) increasing the polarization RL size, the polarization bands to find the converged values.
2. Repeat the [ALDA](#), [BSE](#), and [LRC](#) calculations for light polarized perpendicular to the wire axis.

References

1. F.Bruneval et al., Phys. Rev. Lett. **94**, 219701 (2005)
2. M.Bruno et al., Phys. Rev. B **72**, 153310 (2005)
3. X. Zhao et al., Phys. Rev. Lett. **92**, 236805 (2004)
4. A.Marinopolus et al., Phys. Rev. Lett. **91**, 046402 (2003)

H₂ molecule

by Andrea Marini & Daniele Varsano

The material

- The molecule is along the x direction in the center of a 25 × 25 × 25 (a.u.) cubic cell.
- 1 atom in the cell (1 electrons)
- Plane waves cutoff 14 Hartree (**40000** RL vectors)

Introduction

The H₂ monomer constitutes an example of a perfectly zero dimensional system. The key feature of this chain is that the [polarizability](#) is well described within the ALDA approximation, in contrast with what we have seen the in the previous systems.

[01] Initialization: [01_init](#)(yambo -i)

During the initialization run we need to calculate the closed shells of the Reciprocal space vectors. However if we enter the *OD_h2/yambo* directory and type

```
localhost:>yambo -D
```

```
[RD./SAVE/ns.db1]-----
Bands                : 250
K-points             : 1
G-vectors            [RL space]: 39127
Components          [wavefunctions]: 39127
Symmetries           [spatial+T-rev]: 16
Spinor components    : 1
Spin polarizations   : 1
Temperature          [ev]: 0.000000
Electrons            : 2.000000
- S/N 009258 ----- v.03.00.00 r.000 -
```

we notice that the G-vectors needed to describe the charge of the H₂ molecule are almost 40000! This is a common feature of localized systems. To reduce the computatio time in the *Inputs/01_init* we have defined

```
MaxGvecs= 10000          RL # [INI] Max number of G-vectors planned to use
```

To run the initialization type

```
localhost:>yambo -F Inputs/01_init -J 01_init
```

[02-03] Random-Phase approximation: [02_RPA_no_LF](#)(yambo -o c)

[03_RPA_LF](#)(yambo -o c) [03_RPA_LF_r_space](#)(yambo -o b -y d)

[03_RPA_LF_xl](#)(yambo -o b -y d) [03_RPA_LF_QP](#)(yambo -o b -y d -V 1)

To calculate the polarizability spectrum in the simple independent particle approximation we follow the same scheme described previously. In *Inputs/02_RPA_no_LF* a simple RPA calculation is obtained when

```
NGsBlkXd=1          RL # (Xd) Response block size
```

To run this example type

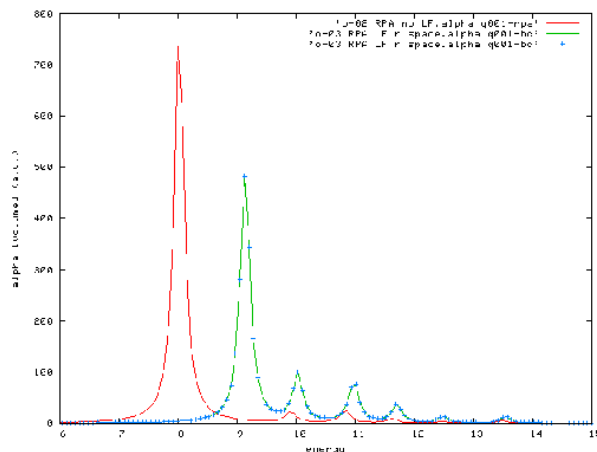
```
localhost:>yambo -F Inputs/02_RPA_no_LF -J 02_RPA_no_LF
```

Now to include Local Fields effects (and later on xc-effects in the ALDA approximation) we **should** increase the *NGsBlkXd* variable. Unfortunately with almost 40000 RL vectors in the charge we would reach the convergence using *NGsBlkXd=2000*. When the TDDFT equation is solved in reciprocal space this value for *NGsBlkXd* corresponds to the inversion of a 2000×2000 matrix, times as many frequencies at which we want to calculate the polarizability. This cumbersome calculation can be avoided using the Bloch representation of the TDDFT equation, corresponding, in yambo, to a BS equation with a modified exchange part that may include the ALDA kernel. To use this option we calculate again the RPA polarizability using the input file *Inputs/03_RPA_LF_r_space* where, because of the RPA, we have

```
BSresKmod= "x" # [BSK] Resonant Kernel mode. (`x`; `c`; `d`)
```

that means: no correlation terms. The next figure confirms that the two procedures lead to very similar results but the real space calculation needs much less cpu-time.

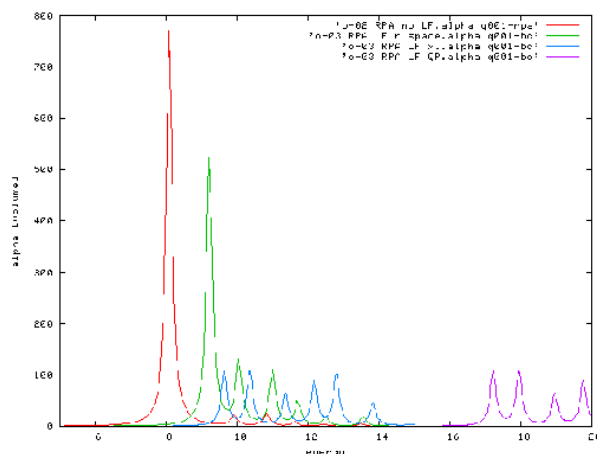
```
localhost:>yambo -F Inputs/02_RPA_LF -J 02_RPA_LF
localhost:>yambo -F Inputs/03_RPA_LF_r_space -J 03_RPA_LF_r_space
```



Still using the Bloch representation of the TDDFT equation we include Local Field effects up to **9000(!)** RL components with and without a QP gap correction of 7.6 eV.

```
localhost:>yambo -F Inputs/03_RPA_LF -J 03_RPA_LF
localhost:>yambo -F Inputs/03_RPA_LF_QP -J 03_RPA_LF_QP
```

obtaining

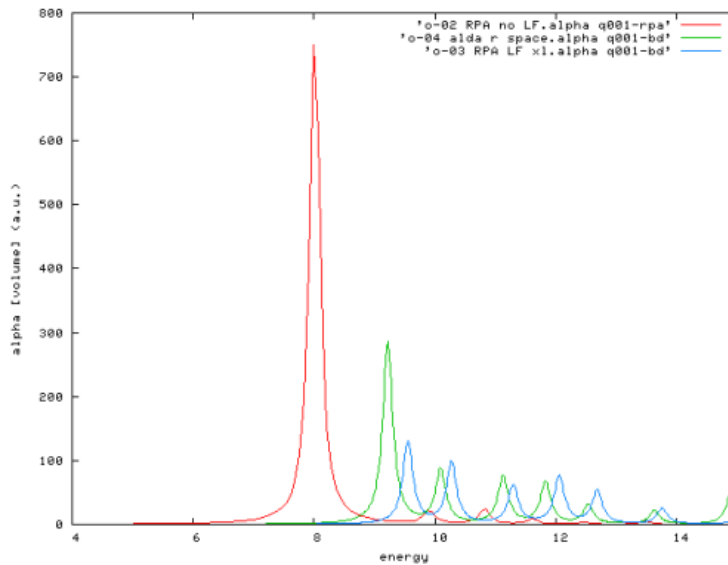


From this plot we see how strong the Local Field effects are in H_2 . This is due to the strong inhomogeneity of the cell charge that has a peak in the cell center while it is very small at the cell boundaries.

[04] ALDA: 04_ALDA_r_space(yambo -o b -t a)

As mentioned before the TDDFT polarizability in the simple ALDA approximation can be obtained in the Bloch representation using the input file *Inputs/04_alda_r_space*

```
localhost:>yambo -F Inputs/04_alda_r_space -J 04_alda_r_space
```



We see the the effect of including xc effects is to counteract the Local Field effects increasing the axial polarizability :

	RPA (no LF)	RPA	ALDA	RPA-QP
$\alpha(\omega=0)$	20.78	9.70	12.51	6.60

While the TDDFT calculations (RPA and ALDA) give a very similar axial polarizability the QP corrections strongly reduce it not in agreement with the Hartree-Fock calculations.

[05] The Statically screened Electron-electron interaction: 05_W(yambo -b)

As a first step to introduce more elaborate approximations for f_{xc} we calculate the statically screened electron-electron interaction of H_2 : using (remember to not use the -J so that the database *ndb.em1s* is stored where all subsequent runs can read it):

```
localhost:>yambo -F Inputs/05_W
```

[06] The Bethe-Salpeter equation, Excitons: 06_BSE(yambo -o b -y d)

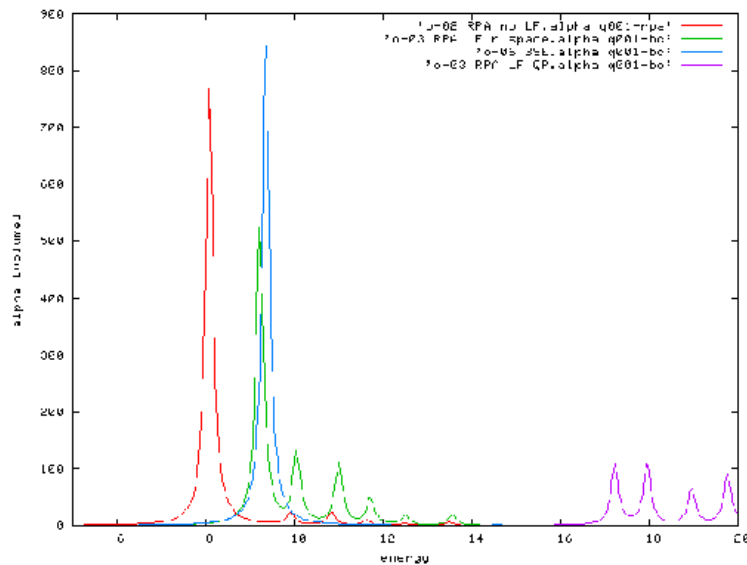
The input file *Inputs/06_BSE* can now calculate the BS polarizability. We notice the use of the BS kernel including exchange scatterings in the coupling part

```
BScplKmod= "x" # [BSK] Coupling Kernel mode. (`x`; `c`; `d`)
```

At difference with 2D and 3D systems, the presence of strong charge inhomogeneity enhances the strength of exchange scatterings between electron-hole pairs with opposite

energy. While generally negligible these terms cannot be neglected in the H_2 molecule.

```
localhost:>yambo -F Inputs/06_BSE -J 06_BSE
```



The resulting BS polarizability is very similar to the ALDA spectrum, showing that **the QP gap correction is almost entirely compensated by the "excitonic" effects.**

Additional Exercises

1. Calculate the absorption spectra like in section [02-03](#) both in RL space and the Bloch representation but using a resonant only kernel. Check the two methods yield the same results, and see the effect of the coupling term (compare it with the linear chain).

References

1. M.van Faassen et al., Phys. Rev. Lett. **81**, 2312 (2000).